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ELECTRON DIFFRACTION STUDY OF THE OXIDATION PROCESS OF THIN FILMS OF INTERMETALLIC COMPOUNDS OF THE SYSTEM NICKEL-ALUMINUM

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ELECTRON DIFFRACTION STUDY OF THE OXIDATION PROCESS OF THIN FILMS OF INTERMETALLIC COMPOUNDS OF THE SYSTEM NICKEL-ALUMINUM

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A method for preparing intermetallic compounds of the nickel-aluminum system in the form of thin films, by vacuum evaporation and condensation of the metal vapor until the percentage composition of the alloy corresponded to a given point of the phase diagram, is described. Electron diffraction studies were used for determining the heat resistance of the alloys and the structure of the oxide films. Simultaneous deposition of aluminum and nickel from two different evaporators on a liquid-nitrogen cooled base resulted not only in reflections characteristic of the two metals but also in reflections characteristic of the compound NiAl.

Investigations on the processes of interaction of the components of an alloy at elevated temperatures are of great practical interest. Nickel-aluminum coatings are heat-resistant at temperatures up to 1000°C, but the brittleness of such coatings at high temperatures constitutes a serious drawback (Bibl.1, 2). Recently, such coatings have been used for protection of steel, nickel, and molybdenum parts of aircraft from corrosion and for protection of metals from oxidation at 550°C (Bibl.3, 4). This system has been studied by other authors by thermographic, microscopic (Bibl.5) and X-ray methods (Bibl.6 - 8).

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* Numbers in the margin indicate pagination in the original foreign text.

Ageyev, Guseva, and Ageyeva studied the electron density distribution in crystals of Al, Ni, and Al-Ni alloys (Bibl.9 - 11), but there are still wide gaps in our knowledge of the questions of heat resistance of these alloys and of the structure of the surface oxide films.

Experimental Part /1165

The specimens for the electron-diffraction study were thin films of alloys prepared by the method of vacuum evaporation and condensation of metal vapor, so that the percentage composition of the alloy corresponded to a given point of the phase diagram. Portions of the metals, accurately weighed on a sensitive microbalance, were placed in tungsten baskets and evaporated in vacuo. The evaporation device consisted of a round-bottom flask with four contacts, a ground joint and liquid-nitrogen traps for freezing out the lubricant vapor. The metals were evaporated simultaneously from two independently operated sources. The same time schedule was selected for the evaporation of each metal. After evaporation, a thin fresh chip of mica with the coating was heated in vacuum to 400 - 450°C. The distance between the weighed portions of the metals was 1 - 2 mm. In this way we obtained uniform distribution of the composition in all directions of the apparatus, as verified by electron-diffraction studies of the alloy from various parts of the flask. The films of alloys, 350 - 400 Å in thickness, were peeled off the mica by the spalling action of the water, and were caught on nickel screen of 0.5 mm mesh, then dried and studied in trans-illumination by the electron-diffraction method.

Alloys of the following compositions were prepared for studying the oxidation processes: 42 wt.% nickel - 58 wt.% aluminum; 57 Ni - 43 Al; 67 Ni - 33 Al; 85 Ni - 15 Al; 90 Ni - 10 Al. From our structural investigations of the alloys,

we can draw the conclusion that the composition of the specimens obtained by this technique fully corresponds to their phase diagram. This is indicated in the electron-diffraction patterns shown in Figs.1, 5, 9. Figure 1, obtained from an alloy of 42 wt.% nickel with 58 wt.% aluminum, shows the reflections characteristic of the compounds $NiAl_3$ and Ni_2Al_3. From Fig.5 it can be concluded that the compounds $NiAl_3$ and Ni_2Al_3 are present, while Fig.9 only indicates the compound NiAl, while Figs.13 and 17 show nickel as predominant; this is due to the fact that these specimens were not sufficiently baked in vacuum during preparation. We used these thin films of alloy to study the structure of the compounds formed from the alloy components, as well as the transition of one structure into the other as a function of the composition at elevated temperature.

In oxidation of the 42 - 58% Al alloy, beginning at 540° C, Fig.2 and the Table (abridged) show not only the lines characteristic for the reflections from the alloy itself, but also reflections corresponding to the aluminum oxide γ-Al_2O_3. At 700° C (Fig.3), there are reflections characteristic only of aluminum oxide, while at 860° C (Fig.4), the double spinel $NiO \cdot Al_2O_3$ begins to appear. At 920° C, there are mostly reflections from aluminum oxide and less from the double spinel. On oxidation of the alloy of composition 57 - 43% Al, at 540° C (Fig.6), the reflections characteristic of the alloy of this composition are accompanied by reflections corresponding to aluminum oxide γ-Al_2O_3; at 700° C (Fig.7), the nickel oxide NiO and the double spinel are formed; at 860° C, reflections characteristic only of the double spinel appear. On oxidation of the alloy 67 - 33% Al (50 atom %) at 540° C (Fig.10), the aluminum oxide γ-Al_2O_3 is formed; at 700° C (Fig.11), the reflections characteristic of the alloy of this composition, are accompanied by reflections characteristic of the nickel

TABLE 1

TABLE OF THE MOST CHARACTERISTIC REFLECTIONS OBSERVED IN THE ELECTRON-DIFFRACTION PATTERNS

Fig. 1; 42 wt. % Ni — 58 wt. % Al			Fig. 5; 57 wt. % Ni — 43 wt. % Al			Fig. 9; 67 wt. % Ni — 33 wt. % Al			Fig. 13; 85 wt. % Ni — 15 wt. % Al			Fig. 17; 90 wt. % Ni — 10 wt. % Al		
I	d	hkil	I	d	hkil	I	d	hkl	I	d	hkl	I	d	hkl
6	3,80 $NiAl_3$	101	5 sc.	3,43 { Ni_2Al_3 / $NiAl_3$	1010 / 111	10	2,03 NiAl	110	10	2,33 Al	111	10	2,03 Ni	111
6	3,66 $NiAl_3$	020	5	2,46 $NiAl_3$	220	3	1,64 NiAl	111	10	2,03 { Ni / Al	111 / 200	8	1,75 Ni	200
5	3,46 Ni_2Al_3	$10\bar{1}0$	9	2,15 $NiAl_3$	112	5	1,437 NiAl	200	4 sc.	1,76 Ni	200	8	1,24 Ni	220
8	2,46 $NiAl_3$	220	10	2,08 { $NiAl_3$ / Ni_2Al_3	131 / $10\bar{1}2$, $11\bar{2}0$	5	1,17 NiAl	211	3	1,24 Ni	220	5	1,06 Ni	311
10 sc.	2,37 $NiAl_3$	031, 221	10	1,915 $NiAl_3$	311, 122	4	0,908 NiAl	310	4	1,21 Al	311	2	1,01 Ni	222
6	2,06 Ni_2Al_3	$10\bar{1}2$, $11\bar{2}0$	5	1,24 Ni_2Al_3	$11\bar{2}3$, $21\bar{3}1$									
9	1,86 $NiAl_3$	230	7	1,16 Ni_2Al_3	$21\bar{3}2$, $30\bar{3}0$									
Fig. 2; 540°			Fig. 6; 540°			Fig. 10; 540°			Fig. 14; 540°			Fig. 18; 540°		
10 sc.	2,03 { γ-Al_2O_3 / Ni_3Al	400 / $10\bar{1}2$, $11\bar{2}0$	3	2,85 { Ni_2Al_3 / γ-Al_2O_3	$10\bar{1}1$ / 220	3	2,86 γ-Al_2O_3	220	7	2,34 Al	111	10	2,37 Al	111
												10	2,03 { NiAl / Al	110 / 200
9	1,90 γ-Al_2O_3	410	10 sc.	2,0 { Ni_2Al_3 / γ-Al_2O_3	$10\bar{1}2$, $11\bar{2}0$ / 400	5	2,34 γ-Al_2O_3	222	10	2,02 NiAl	110			200
												10	1,44 { Al / Al	220
7	1,39 γ-Al_2O_3	441	3	1,63 Ni_3Al	0003, $20\bar{2}1$	10	1,99 γ-Al_2O_3	400	10	1,43 NiAl	200	5	1,22 Al	311
4	1,17 { Ni_3Al / γ-Al_2O_3	$21\bar{3}2$, $30\bar{3}0$ / 631	8	1,38 γ-Al_2O_3	441	9	1,92 γ-Al_2O_3	410	3	1,23 Al	311			211
			6	1,15 Ni_2Al_3	$21\bar{3}2$, $30\bar{3}0$	10	1,36 γ-Al_2O_3	441	3	1,17 { NiAl / Al	211 / 222	5	1,17 { NiAl / Al	222
Fig. 3; 700°			Fig. 7; 700°			Fig. 11; 700°			Fig. 15; 700°			Fig. 19; 700°		
9	1,97 γ-Al_2O_3	400	10	2,40 { $NiAl_2O_4$ / NiO	311 / 111	10	2,40 NiO	111	2	2,85 NiAl	100	10	2,39 NiO	111
10	1,39 γ-Al_2O_3	441	7	2,075 NiO	200	9	2,08 NiO	200	10 sc.	2,42 NiO	111	10	2,05 { NiO / NiAl	200 / 110
3	1,17 γ-Al_2O_3	700	10	2,00 $NiAl_2O_4$	400	6	2,03 NiAl	110	10 sc.	2,03 { NiAl / NiO	110 / 200	10	1,46 NiO	220
4	1,13 γ-Al_2O_3	631	5	1,47 NiO	220	8	1,476 NiO	220	10	1,468 NiO	220	3	1,42 NiAl	200
3	0,99 γ-Al_2O_3	800	10	1,41 $NiAl_2O_4$	440	7	1,42 NiAl	200	10	1,418 NiAl	200	8	1,25 NiO	311
Fig. 4; 860°			Fig. 8; 860°			Fig. 12; 860°			Fig. 16; 860°			Fig. 20; 860°		
5	4,62 { $NiAl_2O_4$ / γ-Al_2O_3	111 / 111	7	2,82 $NiAl_2O_4$	220	6	2,66 $NiAl_2O_4$	220	4	4,68 $NiAl_2O_4$	111	4	2,84 $NiAl_2O_4$	220
8	2,82 { $NiAl_2O_4$ / γ-Al_2O_3	228 / 220	10	2,42 $NiAl_2O_4$	311	10	2,43 $NiAl_2O_4$	311	5	2,85 $NiAl_2O_4$	220	10 sc.	2,43 { $NiAl_2O_4$ / NiO	311 / 111
9 sc.	2,41 { $NiAl_2O_4$ / γ-Al_2O_3	311 / 311	10	2,0 $NiAl_2O_4$	400	8	2,09 NiO	200	10	2,42 $NiAl_2O_4$	311	10 sc.	2,08 { NiO / $NiAl_2O_4$	200 / 400
10 sc.	2,01 { $NiAl_2O_4$ / γ-Al_2O_3	440 / 440	8	1,54 $NiAl_2O_4$	333	7	2,01 $NiAl_2O_4$	400	8	2,086 NiO	200	8	1,48 NiO	220
6	1,94 γ-Al_2O_3	410	10	1,42 $NiAl_2O_4$	440	7	1,47 NiO	220	8	2,004 $NiAl_2O_4$	400	5	1,42 $NiAl_2O_4$	440
10 sc.	1,40 { γ-Al_2O_3 / $NiAl_2O_4$	411 / 440	10	1,15 $NiAl_2O_4$	444	7	1,43 $NiAl_2O_4$	440	8	1,479 NiO	220	7	1,26 NiO	311

* I = Observed intensity, evaluated on the scale of ten; d = size of screen mesh; hkli = index of reflection.

** Commas denote decimal points.

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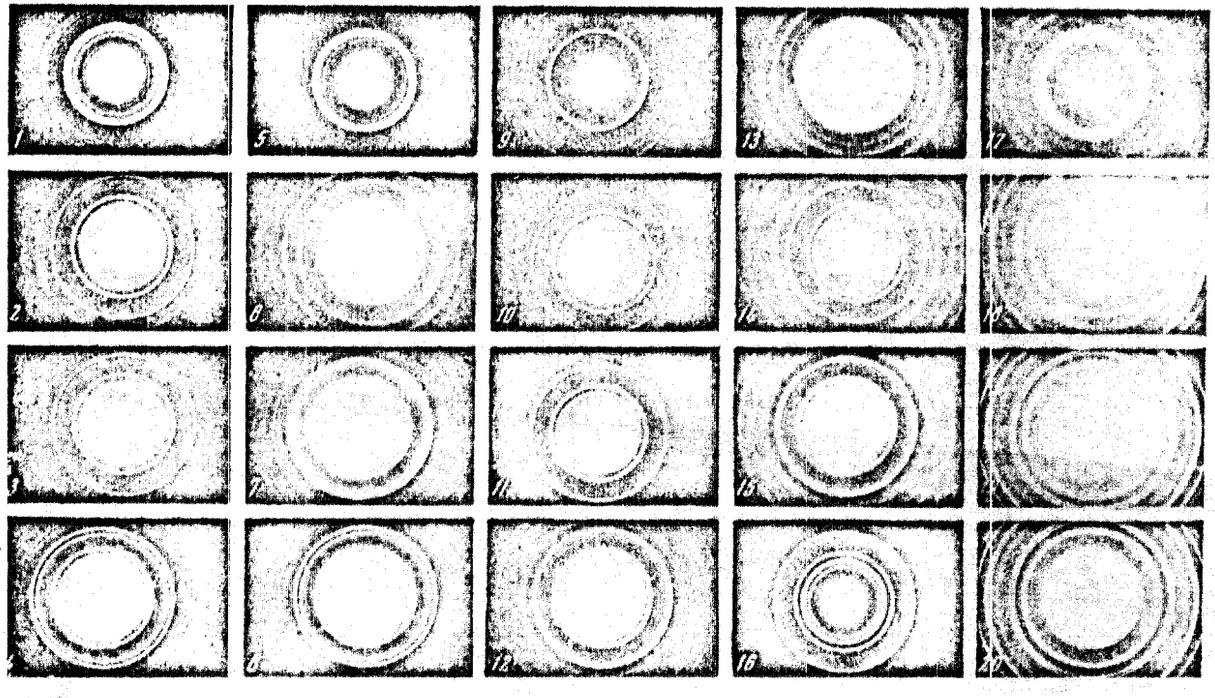

Figs.1 – 20.

oxide NiO; while at 860°C (Fig.12), we see reflections corresponding to nickel oxide and to the double spinel; at 920°C, the pattern is the same. On oxidation of the alloy 85 - 15% Al at 540°C (Fig.14), the reflections characteristic for the alloy NiAl are supplemented by reflections corresponding to aluminum itself; at 700°C (Fig.15), we observe reflections characteristic of the compound NiAl and of nickel oxide, and at 860°C (Fig.16), reflections characteristic of nickel oxide and the double spinel; at 920°C, the pattern is the same. On oxidation of the alloy 90 - 10% Al, beginning at 540°C (Fig.18), the compound NiAl /1167 is formed and reflections characteristic of aluminum are observed; at 700°C, reflections corresponding to nickel oxide and the compound NiAl appear; at 860°C (Fig.20), together with reflections characteristic of NiO there are also reflections corresponding to the double spinel.

During our study, we found that the alloy 67 - 33% (50 at.%) distills in vacuo. After atomizing a small specimen of industrial alloy of this composition in vacuo and taking electron-diffraction transillumination patterns from the resultant film, only the lines characteristic of reflection of this alloy were detected. In our apparatus, the weighed nickel specimen, heated to the melting point, is kept in contact with the weighed aluminum specimen, melting and coalescing with it, which results in a drop of alloy that melts and evaporates at a higher temperature. The electron-diffraction pattern taken from the thin film is the same as in the former case. When an alloy of this composition is evaporated on a base placed in a Dewar with liquid nitrogen (distance between evaporator and base, 90 mm), all reflections correspond to the compound NiAl. On simultaneous vacuum deposition of weighed portions of aluminum and nickel (50 at.%) from two different evaporators onto a base cooled with liquid nitrogen, not only reflections characteristic of these metals were present but also

those characteristic of the compound NiAl.

Conclusions

1. A method of preparing intermetallic compounds in the form of thin films has been developed.

2. The phase composition of oxide films formed on heating to 900°C was determined for five specimens with varying nickel and aluminum contents.

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